UDC 666.11.01:539.213.1:535.3

CERTAIN PHYSICAL PROPERTIES OF BINARY GLASSES DEPENDING ON THEIR STRUCTURAL SPECIFICS

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Translated from Steklo i Keramika, No. 1, pp. 8 – 11, January, 2005.

The concept of structural elements, whose interaction determines glass properties, is used to interpret the regularities of the dependence of the refractive index in binary glass on glass composition, certain results of the mass-spectrometric analysis of the glasses vapor in the $Rb_2O - B_2O_3$ system, and the data on small angle x-ray scattering for glasses in the $Na_2O - SiO_2$ and $Li_2O - SiO_2$ system. Methods for estimating the refractive index of binary glasses depending on their composition and structure are proposed and examples of such calculations for alkali-silicate glasses are given.

Describing physical properties of glasses using the concept of "structural elements" (SE) has been useful in establishing the dependence of the density of a binary system on the ratio between its components [1]. The structural element here is understood as a steady set of atoms retaining its individual properties under various ratios between the system components. The composition of a SE is expressed through the molar content of its components and, therefore, in contrast to molecules, may contain fractions of atoms. The latter means that the same atom belongs to several elements. For instance, considering $0.2Na_2O \cdot 0.8SiO_2$ as the formula of a structural element we see that each element contains 2/5 sodium atom, 4/5 silicon atom, and 9/5 oxygen atoms, i.e., per each 5 structural elements we have 2 atoms of Na, 4 atoms of Si, and 9 atoms of O.

SEs in a system behave in such a way that their properties are manifested not so much through the interaction between their constituent atoms as through the interaction between the elements themselves. For instance, all known glass compositions in the $Na_2O - SiO_2$ system can be split into two composition ranges, in which the glass structure is determined by respective structural elements. In compositions with Na_2O molar content ranging from 0 to 20% the structural elements are the atom groups $0.2Na_2O \cdot 0.8SiO_2$ and SiO_2 which do not mix and thus generate a heterogeneous structure. In compositions with a higher content of the alkali oxide the structural elements are represented by the atomic groups $0.2Na_2O \cdot 0.8SiO_2$ and Na_2O [1], where the heterogeneous elements interact more intensely than the homogeneous ones. Therefore, glasses from the latter composition range have a homogeneous structure and SiO_2 can be considered as the silicon-bearing structural element, since any combination of $0.2Na_2O \cdot 0.8SiO_2$ with the alkali oxide within this range can be represented as the result of the interaction between SiO_2 and Na_2O.

The similarly of a structural element with a molecule consist in the fact that the following concepts are true of SEs: molar mass $M = M_1(1 - x') + M_2 x'$ (M_1 and M_2 are the molar masses of the glass components; x' is the molar content of the second component); molar volume $V = M/\rho$ (ρ is the density of the structural element) and the Avogadro number N_0, i.e., the number of SEs in a molar volume does not depend on their type.

If within a certain composition range, whose bounds are determined by the molar contents of the second component x_1' and x_2', the properties of glasses are determined by the presence of structural elements A and B, then for the composition with the molar content of the second component x' and the structural element B with the molar content x the following relation holds:

$$x = \frac{x' - x_1'}{x_2' - x_1'}.$$

The concept of structural elements makes it possible to eliminate some defects of the quantitative interpretation of experimental results based on small angle x-ray scattering that is given in [2].

The quantitative indicator of the existence of heterogeneities in the electron density[2] distribution over the volume of the material is the average square of the difference of

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[2] Electron density is understood as the number of electrons per volumetric unit of material.

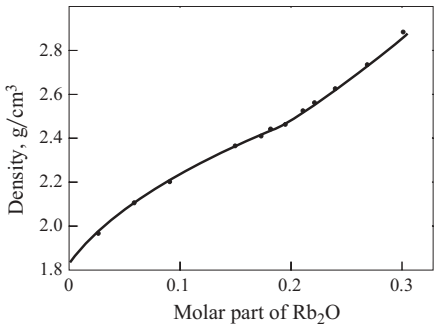

Fig. 1. Dependence of density on molar content of Rb_2O in glasses of $Rb_2O - B_2O_3$ system according to data of M. Kunugi, A. Konishi, S. Takeuchi, and T. Yamate [5].

electron densities $\overline{(\Delta\rho')^2}$ which for a two-phase system depends on the relative volumes of the phases w_A and w_B:

$$\overline{(\Delta\rho')^2} = (\rho'_A - \rho'_B)^2 w_A w_B , \quad (1)$$

where ρ'_A and ρ'_B are the average electron density values of the respective phases.

According to experimental results [2], scattering in sodium silicate glasses reaches its maximum with the molar content of the alkali oxide nearly 11%, whereas the estimated content of this oxide is equal to 7.5%.

In glasses with a heterogeneous structure where each SE forms its own phase, the material density ρ can be expressed via the average densities ρ_A and ρ_B and the relative volumes of each phase:

$$\rho = \rho_A w_A + \rho_B w_B ; \quad (2)$$

the relative volumes of the phases are related to the molar content x of the structural elements B by the "lever rule" [1]:

$$w_A x = w_B (1 - x) k, \quad (3)$$

where $k = V_A / V_B$ is the ratio of the molar volumes of the respective structural elements.

After jointly solving Eqs. (2) and (3) we obtain

$$\left.\begin{aligned} w_A &= \frac{k(1-x)}{k(1-x)+x}; \\ w_B &= \frac{x}{k(1-x)+x}. \end{aligned}\right\} \quad (4)$$

Since in our case glass densities and average electron densities can be regarded as proportional (the deviation from proportionality due to unequal quantities of protons and neutrons in the atomic nuclei of the respective compounds does not exceed 3%), taking into account expression (4), Eq. (1) can be written as follows:

$$\overline{(\Delta\rho)^2} = (\Delta\rho)^2 \frac{kx(1-x)}{[k(1-x)+x]^2} , \quad (5)$$

where $\Delta\rho = \rho_B - \rho_A$.

The maximum heterogeneity corresponds to the composition with $w_A = w_B$. This composition corresponds to the following molar content of the structural element B:

$$x_m = \frac{k}{k+1} .$$

In sodium silicate glass this corresponds to the molar content of the alkali oxide equal to 10.4% ($k = 1.08$, $x_m = 0.52$) and for lithium silicate glasses 18.7% ($k = 1.28$, $x_m = 0.56$), which agrees well with small angle x-ray scattering data [2].

Since in glasses with a heterogeneous structure the value $\Delta\rho$ is related to the interaction index ρ_{AB} (Eq. 4 in [3]), expression (5) can be transformed as follows:

$$\overline{(\Delta\rho)^2} = \rho_{AB}^2 \frac{kx(1-x)}{(k-1)^2} ,$$

i.e., ρ_{AB}^2 in this case can be also regarded as the extent of the heterogeneity of the system.

In the system of alkali-borate glasses $Rb_2O - B_2O_3$ the structure is homogeneous within the range of the molar content of rubidium oxide from 0 to 20%, and B_2O_3 and Rb_2O can be regarded as structural elements, whereas with a higher rubidium content the dependence of glass density on its composition points to the presence of inhomogeneities (Fig. 1). This means that in Eq. (1) from [1]

$$\rho = \rho_A (1 - x) + \rho_B x + \rho_{AB} x (1 - x)$$

the interaction index ρ_{AB} is positive for compositions from the first composition range and negative for the second composition range. Within the first range the molar contents of the structural elements and the system components coincide, since the components themselves act as SEs. In the second range ($x > 0.2$) the role of structural elements is played by the compounds $0.2Rb_2O \cdot 0.8B_2O_3$ and $0.5Rb_2O \cdot 0.5B_2O_3$, whereas the interaction between heterogeneous SE is weaker than between the homogeneous ones. As a result we have a heterogeneous structure with a loosening effect of Rb_2O ($\rho_{AB} < 0$).

The mass-spectrometric analysis of the vapors of the $Rb_2O - B_2O_3$ system at 950 – 1220 K in [4] established the presence of $RbBO_2$, $(RbBO_2)_2$ molecules and at 1300 K the presence of B_2O_3 and Rb as well. These data can be interpreted in the context of the concept of structural elements discussed above. Within the composition range with a homogeneous structure ($0 < x < 0.2$) the bonds between the heterogeneous SEs are so strong that their content in the gaseous phase at the specified temperatures is insignificant. Within the composition range with a heterogeneous structure ($x > 0.2$) the gaseous phase was observed to contain structural elements $0.5Rb_2O \cdot 0.5B_2O_3$ ($RbBO_2$ molecules) and their associations $(RbBO_2)_2$. Their prevalence in the gaseous phase shows that the bonds between them in the condensed phase is the weakest of all registered bonds. In any case

within a temperature interval up to 1200 K no other SEs are registered. This can be explained by the fact that a SE evaporating in the gaseous phase can be represented only by a molecule with the same stoichiometry, i.e., at least five $0.2Rb_2O \cdot 0.8B_2O_3$ elements should associate to form a $Rb_2B_8O_{13}$ molecule, which is hardly probable. At higher temperatures, along with $Rb_2B_2O_4$ molecules, the products of their decomposition (B_2O_3 and Rb_2O) are registered in the vapor and the latter molecule, in turn, decomposes into Rb and O.

With respect to optical properties, any material is a combination of oscillators with a set of natural frequencies ω_{0j}, whose forced oscillations in an electromagnetic field determine the conditions of the wave propagation in the material. If the oscillators are electrons of a single atom or of several interacting atoms, in particular, all atoms constituting the material, their natural frequencies lie within the visible or ultraviolet range. If a material consists of recurrent elements, its optical properties are determined by the properties of these elements and the number of elements per volume unit.

The description of the optical properties of a material is based on its dispersion ratio, which in the weak absorption range acquires the form of the Lorentz-Lorentz formula

$$\frac{n^2-1}{n^2+2} = \frac{1}{3}\sum_i N_i \alpha_i, \tag{6}$$

where n is the refractive index; N_i is the number of structural elements of the type i per volume unit; α_i is the electron polarizability of the structural element of the same type.

Summation is implemented in accordance with the number of types of structural elements present in the material.

If the system consist of SEs of one type, instead of expression (6) we can write

$$3L = N\alpha, \tag{7}$$

where

$$L = \frac{n^2-1}{n^2+2}. \tag{8}$$

If the system contains structural elements of both types occupying the relative volumes w_A and w_B, instead of expression (7) we can write

$$3L = N_A \alpha_A + N_B \alpha_B = N'_A \alpha_A w_A + N'_B \alpha_B w_B,$$

where the nonprimed N_A and N_B are the numbers of structural elements pet volume unit containing both phases, and the primed symbols are the numbers of elements in a volume unit occupied by the phase formed by the structural element of the corresponding type.

Taking into account formula (8) we obtain

$$L = L_A w_A + L_B w_B, \tag{9}$$

where L_A and L_B are the values L from formula (8) for the phase formed by the respective structural element.

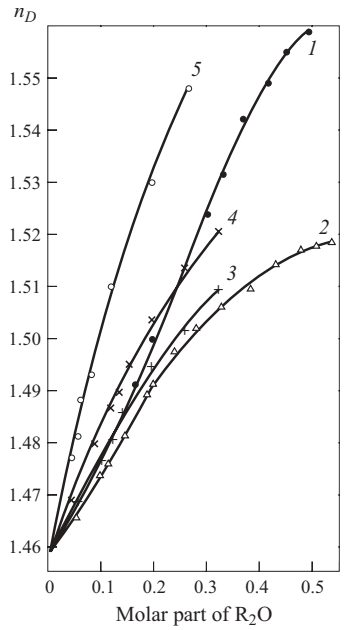

Fig. 2. Dependence of refractive index n_D on molar content of alkali oxide R_2O in alkali-silicate glasses [6]: *1*) Li_2O (S. K. Dubrovo, Yu. A. Shmidt); *2*) Na_2O (G. V. Morey, H. E. Mervin); *3*) K_2O (Yu. A. Shmidt, Z. D. Alekseeva); *4*) Rb_2O (Yu. A. Shmidt, Z. D. Alekseeva); *5*) Cs_2O (Yu. A. Shmidt, Z. D. Alekseeva).

Dependences of w_A and w_B on glass composition are given by expressions (4).

Thus, to describe the optical properties of heterogeneous glasses, we use the formula whose structure coincides with that of expression (2) determining the dependence of glass density on its composition. One has just to replace ρ by L.

As the number of structural elements in a volume unit is proportional to density, formula (6) from [3] can be used as well for the dependence of L on the molar content of the structural element B when replacing ρ by L:

$$L = L_A(1-x) + L_B x + L_{AB} x(1-x), \tag{10}$$

where $L_{AB} = \Delta L_A + \Delta L_B$; $\Delta L_A = L'_A - L_A$; $\Delta L_B = L'_B - L_B$.

In this case the nonprimed values belong to the SE surrounded by the same elements and primed values belong to the SE surrounded by elements of the different type. This makes it possible to describe the optical properties of glasses from the composition range with the homogeneous structure. The results of such description of some glasses are shown in Fig. 2.

All calculations were performed with values L that are related to the refractive index by relation (8). At the same time the calculations used experimental values of n_D given by various authors published in [6]. The calculations for glasses with the heterogeneous structure were performed using formula (9) where the boundary values were taken from published data. For the compositions with the homogeneous structure, calculations in accordance with expression (10) are based on the parabolic equalizing of the values L correspond-

TABLE 1

System	Range*	Structural elements	L_B	L_{AB}	$\sigma \times 10^4$	Experimental data [6]
$Li_2O - SiO_2$	$0 - \frac{1}{3}$	$SiO_2, \frac{1}{3} Li_2O \cdot \frac{2}{3} SiO_2$	0.310	Calculation based on formula (9)	5	S. K. Dubrovo Yu. A. Shmidt
	$\frac{1}{3} - 1$	SiO_2, Li_2O	0.335	0.0775	5	
$Na_2O - SiO_2$	$0 - \frac{1}{5}$	$SiO_2, \frac{1}{5} Na_2O \cdot \frac{4}{5} SiO_2$	0.289	Calculation based on formula (9)	4	G. V. Morey H. E. Mervin
	$\frac{1}{5} - 1$	SiO_2, Na_2O	0.291	0.0822	1	
$K_2O - SiO_2$	0 – 1	SiO_2, K_2O	0.296	0.0843	2	Yu. A. Shmidt
$Rb_2O - SiO_2$	0 – 1	SiO_2, Rb_2O	0.279	0.1340	2	Z. D. Alekseeva
$Cs_2O - SiO_2$	0 – 1	SiO_2, Cs_2O	0.228	0.2840	6	

* The "Range" column gives the boundary values of molar content of the alkali component in glasses whose properties are determined by structural elements specified in the next column.

ing to the respective experimental values of n_D. This yielded the parameters L_A, L_B, and L_{AB}. The calculation curves were obtained by a reverse conversion from the estimated values of L to the estimated values of n according to the following formula:

$$n = \sqrt{\frac{2L+1}{1-L}} .$$

Table 1 gives the parameters used in the calculation of the curves, as well as the mean quadratic deviations σ of estimated values from experimental values for each system:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{l} (n_i - n_i^*)^2}{l(l-1)}} ,$$

where l is the number of experimental correlation points; the asterisk designates the experimental values of the refractive index taken from reference book [6]; they serve for comparison with the estimated values obtained by parabolic leveling (formula (10)) or according to formula (9).

It can be seen from the data in Table 1 that silica acts as the structural element A in all systems considered and the following values are accepted for silica: $n_A = 1.459$, $L_A = 0.273$. The values used in the calculation of the relatives volume according to formulas (4) are: for lithium-silicate glasses $k = 1.28$ and for sodium silicate glasses $k = 1.08$. The deviations of the estimated values from the experimental data are within the measurement error limits (Fig. 2 and Table 1).

Thus, formulas are proposed which make it possible to estimate the refractive index of a binary glass with a high accuracy.

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